

Properties of radiation curable hyperbranched polyurethane acrylate from palm oil oleic acid

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Abstract Radiation curable hyperbranched urethane acrylate (HBUA) from oleic acid of palm oil was synthesized aided by *p*-toluene sulfonic acid as a catalyst. This mixture was then used as the core (HBP-1) and reacted with palm oil oleic acid to form the hyperbranched polyol (HBP-2). HBUA was prepared by reacting HBP-2 resin with diisocyanate and hydroxyl-containing acrylate monomer with the presence of 0.1–2wt% dibutyltin dilaurate as a catalyst. The reaction was confirmed by several analytical data i.e. hydroxyl value (OHV), Fourier Transform infrared (FT IR) spectroscopy gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy analyses. The HBUA was easily curable when subjected to electron beam (EB) or ultraviolet (UV) radiation.

Key words Radiation, Hyperbranched polymers, Oleic acid, Urethane acrylate

1 Introduction

In recent years, there has been a trend in using vegetable oils as raw materials in resin production. The long fatty acids chains of vegetables oil impart desirable flexibility and toughness to otherwise brittle resin system such as epoxy, urethane and polyester. Linear palm oil based urethane acrylate resin has been employed as a prepolymer in the free radical polymerization with encouraging results^[1]. However the curing speed and hardness of the cured films are considered low as compared to the commercial resins. Hyperbranched polymers recently have attracted many attentions since they could bring benefits of low viscosity, good solubility and highly branching molecular structures which contain a large number of functional end groups and are facile for chemical modifications. Among all classes of acrylic oligomers, urethane acrylates have the highest mechanical strengths and chemicals resistant. The objective of the present work was to synthesize hyperbranched palm oil-based urethane acrylate resin. Hyperbranched

urethane acrylates exhibit very rapid curing rate and lower shrinkage than linear urethane acrylates. The cured films have excellent hardness, high chemical resistivity, good scratch resistance, small amount of residual unsaturation and low extractives^[2,3]. This paper presents synthesis and characterization of urethane acrylates based on second-generation hyperbranched polyester polyol from palm oil oleic acid^[4].

2 Materiale and methods

2.1 Materials

Dipentaerythritol (DPE), 2,2-bis(hydroxymethyl) propionic acid (DMPA), isophorone diisocyanate (IPDI), *p*-toluene sulfonic acid (PTSA) and dibutyltin dilaurate (DBTDL) were supplied by Merck-Schuchardt Germany. 2-hydroxyethyl acrylate (2-HEA) was supplied by Aldrich Chemicals Co., USA. Trimethylolpropane triacrylate (TMPTA) was purchased from UCB Chemicals, Belgium and oleic acid (palm oil source) was obtained from Acid Chemical Co., Malaysia. All chemicals were used as received without further purification.

Supported by financial support by the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) through Scifund mechanism (03-03-01-SF0104)

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Received date: 2012-12-31

2.2 Synthesis of hyperbranched polyester polyol (HBP)

The first generation hyperbranched polyester polyol (HBP-1) was synthesized by melt polycondensation technique. DPE was used as the core and DMPA as the chain extender. The synthesis was derived from established methods described elsewhere^[2,3,8,9]. The reaction was carried out at 130–150°C under nitrogen gas atmosphere in the presence of *p*-TSA as the catalyst (0.4wt% of DMPA). The reaction was monitored periodically by checking the acid value until an endpoint of below 10 mg KOH/g was achieved. The HBP-1 was then reacted with the palm oil oleic acid at 190–220°C and labeled as second-generation hyperbranched polyester polyol (HBP-2). The progress of the reaction was monitored by the determination of the hydroxyl values (OHV).

2.3 Synthesis of hyperbranched polyurethane acrylates (HBUA)

The acrylate terminated urethane hyperbranched prepolymers/resins were prepared by carrying out the reaction in a 250 mL five necked flask equipped with a thermometer, dropping funnel, mechanical stirrer and nitrogen gas inlet. Required amount of IPDI with NCO: OH ratio of 9:1 was reacted with HBP-2 at 40–75°C for 3 h with the presence of 0.1%–2.0% DBTDL as the catalyst, as described in our earlier work^[1] NCO terminated hyperbranched polyurethane (PU) prepolymers from HBP-2 was produced. 2-HEA was dropped into the flask with the same ratio of NCO. The synthesis procedure followed was derived from established methods described elsewhere in literature^[5]. Dioxane was added to the flask in order to control the viscosity. The progress of the reaction was monitored by observing the consumption or disappearance of –N=C=O (IPDI) and –OH (HBP-2) groups at approximately 2250–2270 cm^{−1} and 3400–3500 cm^{−1} respectively^[1,6,7,8].

2.4 Electron beam (EB) curing of HBUA – based formulations

The prepolymers (HBUA) were dissolved in acrylate monomer such as TMPTA to reduce the viscosity. The coating formulations were prepared at least one day

prior to curing. The formulated resins were coated on to glass plates using a manual bar coater (RDS 30, Japan), and then irradiated with a 200 keV electron beam machine, Curetron type EBC-200-AA2 (supplied by Nissin High Voltage, Japan) with accelerating voltage of 200 keV, beam current at 2 mA and dose rate of 10 kGy/pass.

2.5 Characterization of the resin

FT IR spectroscopy analysis was carried out using a spectrometer model Perkin Elmer Spectrum 2000. A drop of each sample was spread into a thin layer on the NaCl cells. The samples were scanned at wave numbers ranging from 4000 cm^{−1} to 400 cm^{−1}. The molecular weight (M_w) distributions were determined using Polymer Laboratories GPC, Model PL-GPC 50 Plus with PLgel 10 μm Mixed-B column. Tetrahydrofuran, 1.0 mL/min, was used as the mobile phase. Calibration was carried out by linear polystyrene of known molecular weight and dispersity. The viscosity of the synthesized resins was measured at 25°C with spindle #42 using a Brookfield Viscometer Model RVTDV-II CP. The ¹³C-NMR spectra were recorded with a JEOL ECP 400 MHz NMR using dimethylsulfoxide (DMSO-*d*₆) as a solvent. Standard method ASTM D4274-99 and MPOB Test Method c2.7: 2004 were used to determine hydroxyl values (OHV) and the acid values (AV) of the HBP, respectively.

2.6 Characterization of the cured resins

2.6.1 Determination of gel contents of cured films

Sample in a form of a thin film was weighed (W_1) in a SUS 304 stainless steel wire-mesh filter size #100 and then placed in a soxhlet extractor. Soxhlet extraction was carried out for at least 24 h in acetone. The residue was then taken out, vacuum dried and weighed until it approached a constant weight (W_2). The gel content was calculated using the following equation:

$$\text{Gel Content \%} = \frac{W_1}{W_2} \times 100$$

where, W_1 is mass of sample after extraction (g), W_2 is mass of sample before extraction (g).

2.6.2 Pencil hardness test

The cured films were subjected to the pencil hardness test using Standard Mitsubishi-Uni Pencil (JIS 5400).

Pencil hardness ranges from 9H-9B with the H end of spectrum being the harder and B obviously the softer.

2.6.3 Determination of thermal properties

TGA analyzer model Mettler Toledo TGA 851 was used to study the thermal decomposition profile of the cured hyperbranched polyurethane acrylate. Sample of about 2–3 mg were placed in an alumina pan and heated at rate of 10°C/min in nitrogen gas atmosphere from 50–550°C.

2.6.4 Morphological studies

Morphology of the cured films HBUA coated on medium density fibreboard (MDF) was investigated using scanning electron microscopy Philip XL-30.

3 Results and discussion

3.1 HBP-1, HBP-2 and HBUA characterization

The FTIR spectra of oleic acid, HBP-1, HBP-2 and HBUA are shown in Fig.1.

HBP-1 resin: FTIR (KBr, cm^{-1}): 3200–3600 cm^{-1} (-OH), 2943 cm^{-1} (-CH₃), 2872 cm^{-1} (-CH₂), 1717 cm^{-1} (C=O), 1464 cm^{-1} (aliphatic, -CH₂), 1371 cm^{-1} (aliphatic, -CH₃-), 1240 cm^{-1} (C-O). ¹³C-NMR (300 Hz, DMSO-*d*₆): δ174.75 ppm (-C-CO-O-), δ70.9 ppm (-C-CH₂-O-), δ65.43 ppm (-CH₂-OH), δ39.5 ppm (-C-C-C-). The presence of these bands indicates the successful reaction between DPE and DMPA to the production of HBP-1. These results confirmed the formation of hyperbranched polyester polyol resin (HBP-1).

HBP-2 resin: FTIR (KBr, cm^{-1}): 3200–3600 cm^{-1} (-OH), 2936 cm^{-1} and 2843 cm^{-1} (CH₃-, -CH₂-); 1744 cm^{-1} (-C=O-); 1468 cm^{-1} (-CH₂-, aliphatic) and 1240 cm^{-1} (-COO-, ester). ¹³C-NMR (300 Hz, CDCl₃): δ174.75 ppm (-C-CO-O-), δ70.9 ppm (-C-CH₂-O-), δ65.43 ppm (-CH₂-OH), δ39.5 ppm (-C-C-C-). The hydroxyl value (OHV) of the HBP-2 was 700 mg KOH/g. The presence of these bands indicated the success of the reaction between HBP-1 and oleic acid to produce HBP-2 resin.

HBUA: FTIR (KBr, cm^{-1}): 3300–3360 cm^{-1} (-NH- bending), 1562 cm^{-1} (-CN stretching), 1635 and 810 cm^{-1} (double bonds of acrylate groups). These suggested that both acrylate and amine groups have been successfully bonded to HBP-2 resin to form.

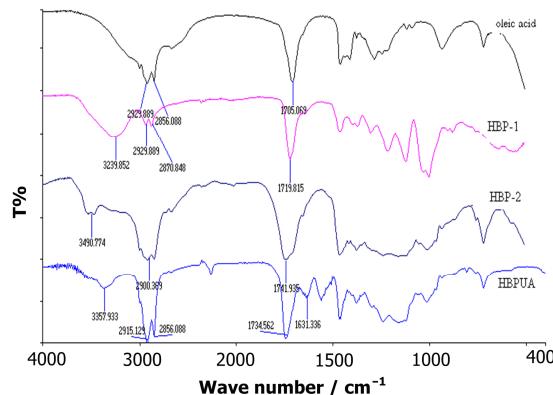


Fig.1 FT IR spectra of oleic acid, HBP-1, HBP-2 and HBUA.

Figure 2 shows the ¹H-NMR spectra of HBUA. A peak at 6.4 ppm was assigned to the acrylic group in HBUA (-NHCO-). The presence of 5.1–5.2 ppm peaks were assigned to the hydrogen atom attach to the unsaturated carbon (-CH=CH-). The peaks at 3.8–4.2 ppm were assigned to the hydrogen atom of methylene connected to ester group (-CH-COO-). These suggested that both acrylate and amine groups have been successfully bonded to HBP-2 resin to form HBUA. The FT IR and ¹H NMR analyses, confirmed that both acrylate and amine groups have been successfully bonded to HBP-2 resin to form HBUA.

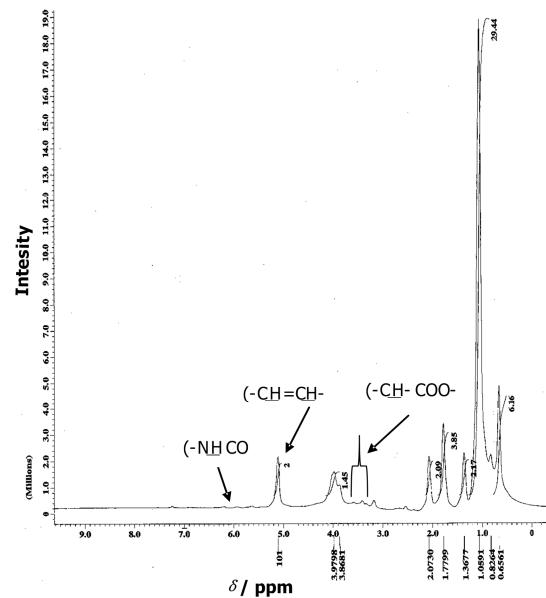


Fig.2 ¹H NMR spectrum of HBUA.

Table 1 summarized data obtained from gel permeation chromatography analysis, viscosity and hydroxyl value (OHV) tests of HBP-2 and HBUA.

The low viscosity implied that HBP-2 and

HBPUA molecules were less entangled due to the spherical shape. One of the most interesting properties of hyperbranched polymers was their high M_w and low

viscosity characteristic in comparison to linear analogue^[3,9]. Low polydispersity index obtained justified these findings.

Table 1 Characteristics of HBP-2 and HBPUA

Samples	M_n	M_w	Polydispersity Index, $I=M_w/M_n$	Viscosity	OHV, mg KOH/g
HBP-2	13 692	40 755	2.976	680	700
HBPUA	22 281	59 753	2.68	15 430	8.5

3.2 Characterization of the cured resins

EB curing of HBPUA: HBPUA contained unsaturated sites which were capable to undergo polymerization through the double bond. A thin layer of HBPUA was applied on a glass plate and

polymerized to a solid film upon exposure to EB radiation. The prepolymer HBPUA cured at 100 kGy. Fig.3 showed the FTIR spectra of the cured HBPUA sample and did not show any peak representing acrylate group at 1634 cm^{-1} and 810 cm^{-1} since it has undergone polymerization on exposure to EB radiation.

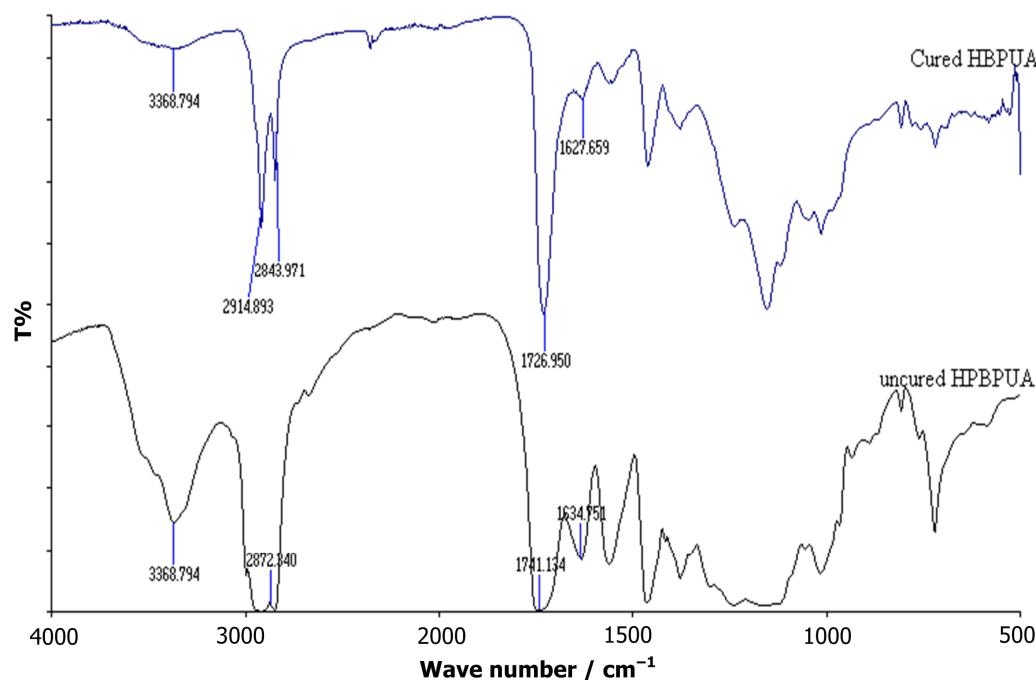


Fig.3 FT IR spectra of cured HBPUA and uncured HBPUA.

Properties of the cured film: The formulations of HBPUA were developed based on the radiation dose and its effect on the hardness and gel content. These were summarized in Table 2. An increase in the amount of TMPTA from 40% to 60% resulted in an increase in pencil hardness and gel

content of the cured films. TMPTA having multifunctional acrylic group formed cross linking with HBPUA producing hard films. Higher reactivity of the acrylates in TMPTA contributing high degree of cross linking and made it possible to use less radiation dose for curing.

Table 2 Effect of TMPTA and electron beam radiation onto pencil hardness and gel content

Formulations	Radiation Dose— /kGy	Pencil hardness Index	Gel content / %
HBPUA	100	4B	60
HBPUA:TMPTA(6:4)	50	B	70
HBPUA:TMPTA(5:5)	50	F	72
HBPUA:TMPTA(4:6)	50	2H	80

The TGA and DTG thermograms of the HBPUA formulations were as shown in Fig.4. The thermal decomposition of HBPUA started at 200°C with 98% weight loss. The weight loss of HBPUA-1: TMPTA at the ratio of 6:4 was 95% at temperature of 200°C. Fig.5 showed that thermal stability of HBPUA increased in the presence of TMPTA, i.e. T_{max} of 450°C was shifted to a higher temperature i.e. T_{max} 455°C. This indicated that the thermal stability of HBPUA improved by TMPTA monomer. The effect was believed to be due to the induced chemical interaction in the form of cross linking.

Figure 6 exhibited the interfacial adhesion between HBPUA/TMPTA and MDF as shown in the scanning electron micrographs (SEM). The morphology showed good interaction between cured film and substract.

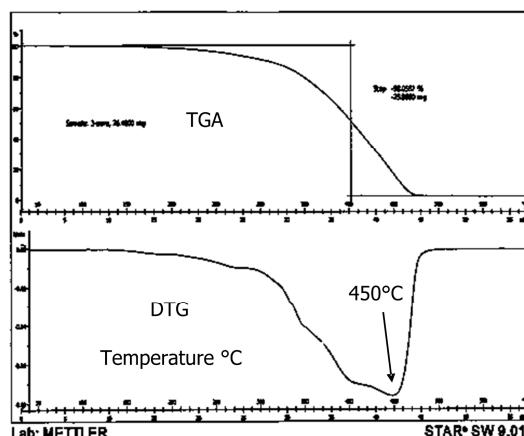


Fig.4 TGA and DTG thermograms of HBPUA.

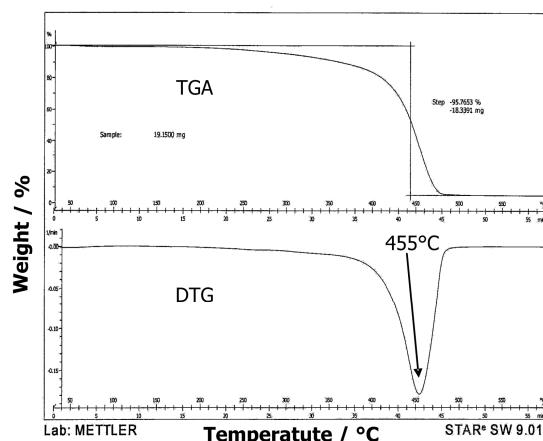


Fig.5 TGA and DTG thermograms of HBPUA/TMPTA.

4 Conclusion

Hyperbranched polyurethane acrylate prepolymers/resins (HBPUA) were synthesized from oleic acid of palm oil source. HBPUA cured films exhibited high cross-linking density or gel content with high pencil hardness index. The thermal decomposition study of cured films HBPUA shows good thermal stability and negligible weight loss up to 450°C. The hyperbranching acrylate structures offer an advantage for various applications for coating industries such as wood coatings, printing inks, adhesives (PSA) etc.

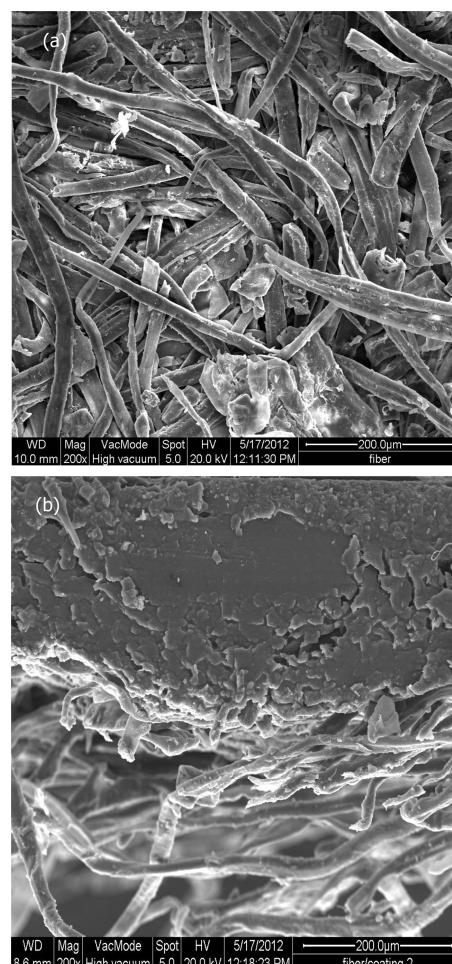


Fig.6 SEM micrographs of (a) MDF and (b) cured film of HBPUA/TMPTA on MDF.

References

- 1 Mohd Hilmi M, Rosley CI, Mek Zah S, et al. Malaysian Patent, 2011, MY-142814-A.
- 2 Dzunuzovic E, Tasic S, Bozic B, et al. Progress Org Coat, 2005, **52**: 136–143.
- 3 Yates, C R, Hayes W. Eur Polym J, 2004, **40**: 1257–1281.

- 4 Mek Z, Khairiah B, Mohd H, *et al.* J Nucl Relat Technol, 2010, **7**: 38–48
- 5 Holman R, Oldring P. UV & EB Curing for Printing Inks, Coatings & Paints, SITA Technology Publisher, London, 1988.
- 6 Silverstein R M, Clayton B, Morrill T C. Spectrometric Identification of Organic Compounds, John Wiley, Singapore, 1991.
- 7 Wong C S, Khairiah H B. [online]. Available at: doi:10.4236/msa.2012.32012, <http://www.SciRP.org/journal/msa>, 2012, **3**: 78–86.
- 8 Badri KH, Ahmad SH, Zakaria, S. J Appl Polym Sci, 2001, **82**: 827–832.
- 9 Bat E, Gunduz G, Kisakurek D, Akhmedov I M. Progress Org Coat, 2006, **55**: 330–336.
- 10 Gang X, Shi W, Gong M, *et al.* Eur Polym J, 2004, **40**: 483–491.
- 11 Gao C, Yan D. Progress Polym Sci, 2004, **29**: 183–275.
- 12 Jena K K, Chattopadhyay D K, Raju KVSN. Eur Polym J, 2007, **43**: 1825–1837.
- 13 Lomolder R, Plogmann P, Speler, P. J Coat Technol, 1997, **69**: 51–57.